

SUPPLEMENTARY MATERIAL

Revisiting isothermal effectiveness factor equations for reversible reactions

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SM1. Calculating effective diffusivities in porous catalysts

In this work, effective diffusivities were calculated using two different approaches to evaluate their impact on the analytical effectiveness factor. The first approach is based on the Rios, et al., [1] model and takes into consideration mixture non-idealities using activity coefficients, whereas the second assumes mixtures are ideal and is based on Bird, et al., [2] equations. The equations associated with each model are briefly summarized in this section.

SM1.1. Non-ideal effective diffusivities model equations (Rios, et al., [1])

Given a mixture with n components, the effective diffusivities in solution, $D_{ef,i}^{mix}$, of the first $n - 1$ species are given by:

$$\frac{1}{D_{ef,i}^{mix}} = \sum_{j=1}^{n-1} D_{ij}^{inv} \frac{\vec{J}_j}{\vec{J}_i} \quad (SM1)$$

where \vec{J}_j is the molar diffusion flux vector of component j and D_{ij}^{inv} represents the ij entry of the inverse of matrix $[D]$, defined as the product of two matrices:

$$[D] = [B]^{-1}[\Gamma] \quad (SM2a)$$

$$B_{ii} = \frac{x_i}{\mathfrak{D}_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{\mathfrak{D}_{ij}} \quad (SM2b)$$

$$B_{ij} = -x_i \left(\frac{1}{\mathfrak{D}_{ij}} - \frac{1}{\mathfrak{D}_{in}} \right) \quad (SM2c)$$

$$\Gamma_{ij} = \delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{P,T,x_k [k=1,2,\dots,n-1,k \neq j]} \quad (\text{SM2d})$$

$$\delta_{ij} = \frac{\partial x_i}{\partial x_j} = \begin{cases} \delta_{ij} = 0, & i \neq j \\ \delta_{ij} = 1, & i = j \end{cases} \quad (\text{SM2e})$$

where B_{ii} and B_{ij} are the diagonal and off-diagonal elements of $[B]$, respectively, Γ_{ij} is the ij element of $[\Gamma]$, γ_i is the activity coefficient of i , x_i is the liquid phase mole fraction of i , and \mathfrak{D}_{ij} is a Maxwell–Stefan diffusion coefficient.

The effective diffusivity of the n^{th} component is calculated with:

$$\frac{1}{D_{\text{ef},n}^{\text{mix}}} = - \sum_{j=1}^{n-1} \frac{1}{D_{\text{ef},j}} \frac{\vec{J}_j}{\vec{J}_n} \quad (\text{SM3})$$

SM1.2. Ideal effective diffusivities model equations

For ideal solutions, Bird, et al., [2] proposed the following equations for the effective diffusivities of a species i in a mixture of n components:

$$D_{\text{ef},i}^{\text{Mix,Ideal}} = \frac{\vec{N}_i - \vec{N}_T x_i}{\vec{N}_i \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{\mathfrak{D}_{ij}} - x_i \sum_{\substack{j=1 \\ j \neq i}}^n \frac{\vec{N}_j}{\mathfrak{D}_{ij}}} \quad (\text{SM4})$$

where \vec{N}_i is the molar flux of i and \vec{N}_T is the total molar flux. This expression can be derived from the equations presented in SM1.1. by setting $[\Gamma] = [I]$ (identity matrix) and manipulating resulting expressions.

SM1.3. Case studies specifics

Given the relationship between \vec{N}_i and \vec{J}_i , i.e., $\vec{N}_i = \vec{J}_i + x_i \vec{N}_T$, the required ratios \vec{J}_j / \vec{J}_i to calculate effective diffusivities can be computed from the reaction stoichiometry.

- Case 1—esterification of ethanol with acetic acid ($A + B \rightleftharpoons C + D$): since the sum of stoichiometric coefficients is zero, $\vec{N}_T = 0$, which yields $\vec{N}_i = \vec{J}_i$. Then, the ratios \vec{J}_j / \vec{J}_i are independent of the mixture composition and are given by:

$$\frac{\vec{J}_j}{\vec{J}_i} = \begin{cases} 1, & j \text{ and } i \text{ are both products or reactants} \\ -1, & \text{otherwise} \end{cases} \quad (\text{SM5})$$

- Case 2—acetal synthesis ($2A + B \rightleftharpoons C + D$): using the reaction stoichiometry, it is possible to express the molar flux of each component in terms of the molar flux of a reference species A . Knowing that $N_B = 0.5 N_A$, $N_C = -0.5 N_A$ and $N_D = -0.5 N_A$ yields $N_T = 0.5 N_A$, thus:

$$J_A = N_A(1 - 0.5x_A) \quad (\text{SM6a})$$

$$J_B = \frac{1}{2}N_A(1 - x_B) \quad (\text{SM6b})$$

$$J_C = -\frac{1}{2}N_A(1 + x_C) \quad (\text{SM6c})$$

$$J_D = -\frac{1}{2}N_A(1 + x_D) \quad (\text{SM6d})$$

Then, the following matrix of molar diffusion fluxes can be written:

$$\begin{bmatrix} \frac{J_A}{J_A} & \frac{J_B}{J_A} & \frac{J_C}{J_A} & \frac{J_D}{J_A} \\ \frac{J_A}{J_B} & \frac{J_B}{J_B} & \frac{J_C}{J_B} & \frac{J_D}{J_B} \\ \frac{J_A}{J_C} & \frac{J_B}{J_C} & \frac{J_C}{J_C} & \frac{J_D}{J_C} \\ \frac{J_A}{J_D} & \frac{J_B}{J_D} & \frac{J_C}{J_D} & \frac{J_D}{J_D} \end{bmatrix} = \begin{bmatrix} 1 & \frac{1}{2} \cdot \frac{1 - x_B}{1 - 0.5x_A} & \frac{-1}{2} \cdot \frac{1 + x_C}{1 - 0.5x_A} & \frac{-1}{2} \cdot \frac{1 + x_D}{1 - 0.5x_A} \\ 2 \cdot \frac{1 - 0.5x_A}{1 - x_B} & 1 & -\frac{1 + x_C}{1 - x_B} & -\frac{1 + x_D}{1 - x_B} \\ -2 \cdot \frac{1 - 0.5x_A}{1 + x_C} & -\frac{1 - x_B}{1 + x_C} & 1 & \frac{1 + x_D}{1 + x_C} \\ -2 \cdot \frac{1 - 0.5x_A}{1 + x_D} & -\frac{1 - x_B}{1 + x_D} & \frac{1 + x_C}{1 + x_D} & 1 \end{bmatrix}$$

For binary mixtures at infinite dilution, the Maxwell–Stefan diffusion coefficient is equal to the binary diffusion coefficient, $\mathfrak{D}_{ij}^\infty = D_{ij}^\infty$. By estimating D_{ij}^∞ for each ij pair, the \mathfrak{D}_{ij} for the desired composition is obtained with the following mixing rule:

$$\mathfrak{D}_{ij} = (\mathfrak{D}_{ij}^\infty)^{(1-x_i+x_j)/2} \times (\mathfrak{D}_{ji}^\infty)^{(1-x_j+x_i)/2} \quad (\text{SM7})$$

In this work, the Wilke–Chang equation [3] was employed to calculate D_{ij}^∞ .

SM2. Calculating equilibrium concentrations

The thermodynamic equilibrium constant, K , is given by:

$$K = \prod_j a_{j\text{eq}}^{\nu_j} = \left(\prod_j x_{j\text{eq}}^{\nu_j} \right) \times \left(\prod_j \gamma_{j\text{eq}}^{\nu_j} \right) \equiv K_x K_\gamma \quad (\text{SM8})$$

where ν_j is the stoichiometric and a_j the activity of component j , which for a liquid phase reaction is defined as $a_j = \gamma_j x_j$, in which x_j and γ_j represent the mole fraction and the activity coefficient of component j , respectively, and subscript “eq” denotes equilibrium.

The value of K at the working temperature is obtained from thermodynamic data using the Van’t Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H_R^\circ + \sum_j \nu_j C p_j (T - 298.15)}{R_g T^2} \quad (\text{SM9})$$

with $\ln K = -\Delta G_R^\circ / (R_g T_{\text{ref}})$ at $T_{\text{ref}} = 298.15$, where R_g is the universal gas constant, $C p_j$ is the constant pressure heat capacity of component j , and ΔH_R° and ΔG_R° are the standard enthalpy and the Gibbs free energy of reaction, respectively. From equation (SM8), the value of K depends only on temperature, but K_γ is composition-dependent, so the calculation of K_x requires an iterative procedure, described below:

1. In the first iteration, provide an estimate of K_γ , such as $K_\gamma = 1$;
2. Calculate $K_x = K / K_\gamma$;
3. Calculate the equilibrium conversion, X_{eq} , by solving $K_x = \prod_j x_{j_{\text{eq}}}^{\nu_j}$, with:

$$x_{j_{\text{eq}}} = x_{j_{\text{in}}} + \nu_j x_{A_{\text{in}}} X_{\text{eq}} \quad (\text{SM10})$$

in which $x_{A_{\text{in}}}$ is the initial mole fraction of component A (at $t = 0$).

For the type I reaction ($A + B \rightleftharpoons C + D$) with an equimolar feed of reactants, this step is simplified to:

$$X_{\text{eq}} = \frac{\sqrt{K_x}}{1 + \sqrt{K_x}} \quad (\text{SM11})$$

4. Calculate the equilibrium mole fractions using equation (SM10);
5. Compute the activity coefficients of each component, $\gamma_{j_{\text{eq}}}$, at the calculated composition, and then calculate $K_\gamma = \prod_j \gamma_{j_{\text{eq}}}^{\nu_j}$ using an appropriate activity coefficient model (e.g., the UNIFAC model [4]);
6. Using the previously calculated K_γ , repeat steps 2—5 until the algorithm converges, i.e., the variation in X_{eq} between two consecutive iterations is smaller than a specified tolerance:

$$\Delta X_{\text{eq}} < \text{tolerance} \quad (\text{SM12})$$

7. Once the method has converged, X_{eq} is used to calculate $C_{A_{\text{eq}}}$ directly with:

$$C_{A_{\text{eq}}} = C_{A_{\text{in}}} (1 - X_{\text{eq}}) \quad (\text{SM13})$$

which also enables the determination of K_x using the equilibrium mole fractions.

SM3. Wet Amberlyst-15 resin porosity calculation

In the first case study regarding the esterification of ethanol with acetic acid, the Amberlyst-15 catalyst particles were not dried before being used for the reaction. Consequently, the porosity of the wet resin might differ from that of the dry resin, which is typically the value reported in the literature. To account for this, the porosity of wet Amberlyst-15 was estimated with its water-swollen properties given by Badia *et al.* [5], who obtained them using the Inverse Steric Exclusion Chromatography (ISEC) technique. This technique is a variation on the size exclusion chromatography capable of providing information on the microporous structure of a swollen polymer [6]. The porosity is then given by:

$$\varepsilon = 1 - \frac{1}{\rho_{sk}} \times \frac{1}{V_{sp} + V_{pore}} \quad (\text{SM14})$$

where $V_{sp} = 0.765 \text{ cm}^3/\text{g}$ is the specific volume of the swollen polymer, $V_{pore} = 0.616 \text{ cm}^3/\text{g}$ is the volume of the meso-macropores in water-swollen state, $\rho_{sk} = 1.416 \text{ g/cm}^3$ is the skeletal density of the dry resin. Replacing these values (provided by Badia *et al.* [5]) in equation SM14 yields $\varepsilon = 0.489$.

References

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Nomenclature

a_j	activity of component j
C_j	concentration of component j , mol/dm ³
Cp_j	constant pressure specific heat capacity of component j , J/(mol K)
D_{ij}	diffusion coefficient, dm ² /min
\mathring{D}_{ij}	Maxwell-Stefan diffusion coefficient, dm ² /min
G	Gibbs free energy, J/mol
H	enthalpy, J/mol
J_j	molar diffusion flux, mol/(dm ² min)
K	thermodynamic equilibrium constant
K_x	defined in equation (SM8)
K_γ	defined in equation (SM8)
N_j	molar flux, mol/(dm ² min)

R_g	universal gas constant, J/(mol K)
T	temperature, K
t	time, min
V_{sp}	volume of swollen polymer, cm ³ /g
V_p	volume of pores, cm ³ /g
X_{eq}	equilibrium conversion
x_j	liquid phase mole fraction of component j

Greek letters

γ	activity coefficient
Δ	variation of a thermodynamic property
ν_j	stoichiometric coefficient of component j
ρ_{sk}	skeletal density, g/cm ³

Subscripts

ef	effective
eq	equilibrium
in	initial
R	reaction
Ref	reference

Superscripts

inv	inverse
mix	mixture
∞	infinite dilution
$^\circ$	standard conditions (1 bar, 298.15 K)